Applied Catalysis B: Environmental 176–177 (2015) 553–558

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Synthesis of activated carbon based heterogenous acid catalyst for biodiesel preparation

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ARTICLE INFO

Article history:
Received 26 January 2015
Received in revised form 15 April 2015
Accepted 20 April 2015
Available online 21 April 2015

Keywords:
Activated carbon
Mesoporous solid acid catalyst
Arylation
Esterification
Biodiesel

ABSTRACT

The present work illustrates the synthesis of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$), obtained from activated carbon (AC) by arylation with 4-sulfobenzenediazonium chloride. The variation of reaction conditions, such as, reaction temperature (20–85 °C) and weight ratio of sulfanilic acid (precursor of 4-sulfobenzenediazonium chloride) to AC (0.14/1–14.00/1) provided $ACPhSO_3H$ with relatively high density of acid sites. The $ACPhSO_3H$ with the highest $PhSO_3H$ density (0.72 mmol H^+/g) was obtained using weight ratio of sulfanilic acid to AC (7.00/1) at 70 °C after 10 min. The catalyst was characterized by means of nitrogen adsorption analysis (average pore diameter 10.1 nm, specific surface area 114 m^2/g, pore volume 0.29 cm^3/g), FT-IR, TG, XRD, FE-SEM and S elemental analysis. The spent catalyst can be easily regenerated recovering its initial density of acid sites. Upon employment in esterification reactions of rapeseed oil fatty acids, $ACPhSO_3H$ showed similar catalytic performance to Amberlyst-15.

1. Introduction

Biodiesel is a biodegradable large scale fuel product manufactured in many countries from renewable feedstock such as vegetable oils [1]. The main properties of biodiesel are close to diesel fuel [2], therefore, it has been successfully used as fuel for commercial diesel engines. Currently, biodiesel is produced from food grade vegetable oils (rapeseed, soybean, sunflower and palm) [3], but it also can be obtained from any raw material containing fatty acids or their glycerides. Alkalis (NaOH, KOH, $NaOCH_3$) are the commonly used homogeneous catalysts for biodiesel production from vegetable oil. The activity of alkaline catalysts is significantly higher than that of acidic catalysts [4]. Nevertheless, acid catalysts are less sensitive to quality of raw material [5] and are suitable for the biodiesel production processes when the raw material contains elevated concentration of free fatty acids and water [1,6]. Homogenous acid catalysts as strong mineral acids (H_2SO_4) provide high yield of biodiesel in the esterification and transesterification reactions [2,7]. The reusability of homogeneous acid catalysts is complicated due to its high solubility in reaction mixture [8]. The high amount of energy is required for catalyst separation, recycling and purification of products, hence increasing the actual cost of biodiesel. The employment of reusable heterogeneous catalysts for biodiesel production allows for a cost minimization and development of low-waste technology. The acidic ion-exchange resins are widely used in industrial processes for different esterification reactions [9]. Industrial grade solid acid catalysts such as Amberlyst-15 and Amberlyst-BD20 [10] have a polymer–based structure, chemically bonded with 4-sulfophenyl ($PhSO_3H$) groups. Amberlyst-15 and Amberlyst-BD-20 have a high $PhSO_3H$ density and suitable textural properties (specific surface area, pore volume and average pore diameter) for esterification of free fatty acids (FFA) in biodiesel production processes. Mesoporous carbon based solid acid catalysts (C_{sac}) can be obtained with wide range of textural properties and relatively high density of sulfo (SO3H) or $PhSO_3H$ groups ensuring the successful conversion of FFA to biodiesel [11,12]. Moreover, the carbon materials or their precursors are low cost feedstock for the C_{sac} preparation, even more increasing its potential for practical application in biodiesel production processes [8]. FFA, FFA tryglicerides and fatty acid alkyl esters can effectively diffuse through C_{sac} structure and reach the functional groups located within the catalyst surface. C_{sac} can be divided in two groups – supported and functionalized catalysts. Functionalized C_{sac} can be obtained via two main approaches – direct sulfonation and sulfonation by alkylation or arylation. Direct sulfonation is the most studied method for the preparation of C_{sac} catalysts. Various carbon precursors, such as glucose [13], microalgae-residues [14], vegetable oil, asphalt [15] and other organic materials can be directly carbonized (400–700 °C) and then sulfonated with conc. H_2SO_4 at 150–210 °C temperature. Furthermore, there is a single step

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http://dx.doi.org/10.1016/j.apcatb.2015.04.043
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method for the preparation of C_{sac} catalyst by partial carbonization and sulfonation (220 °C) of glycerol [16].

The preparation of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$) using reductive arylation is a simple way to obtain catalyst with high total acid density (up to ~2.0 mmol H^+/ g) at low temperature (0–5 °C) [17–20]. For the preparation of $ACPhSO_3H$ catalyst, usually 4-sulfobenzenediazonium salts and as reducing agent H_3PO_2 are utilized. The catalytic activity of $ACPhSO_3H$ on esterification reactions of various lower alcohols with an carboxylic acids such as acetic, hexanoic, decanoic and oleic acid was compared with commercial solid acid catalysts, such as, Amberlyst-15 and Nafion NR50 [18,21]. However, there are no comprehensive data in the literature about arylation of carbon based materials using diazonium salts at temperatures higher than 5 °C (without reducing agent H_3PO_2). Furthermore, the number of investigations using $ACPhSO_3H$ for the preparation of fatty acid methyl esters from feedstock with high content of FFA is limited.

The present study was conducted in order to investigate the effect of different experimental conditions like weight ratio of sulfanilic acid to activated carbon (AC) (0.14/1–14.00/1) and reaction temperature (20–85 °C) on acid density of $PhSO_3H$ groups attached onto AC matrix.

The catalytic effect of $ACPhSO_3H$ (10 wt.%) on esterification reactions of rapeseed oil fatty acids (RFA) and RFA/rapeseed oil (RO) mixture (weight ratio 1/2) were investigated using molar ratio of RFA to methanol (1/20), reaction time (0–7 h) at 65 °C. The mixture of RFA/RO allows the reaction environment to be comparable to the industrial biodiesel production processes when the content of FFA in vegetable oil is elevated. The industrial Amberlyst-15 catalyst, used as reference, was also tested under identical experimental conditions.

2. Experimental

2.1. Materials

Methanol, acetone, $NaNO_2$, sulfanilic acid, benzenesulfonic acid, NaOH with purity ≥98 wt.% and conc. mineral acids HCl (35.8 wt.%) and H_2SO_4 (96.3 wt.%) were purchased from Sigma–Aldrich. Concentrations of mineral acids determined using volumetric analysis acid-base titration. Amberlyst-15 hydrogen form – dry and AC (mesh 20–40) was supplied from Sigma–Aldrich. RFA was derived from RO by hydrolysis reaction with water in presence of H_2SO_4. The main characteristics of RFA and RO are given in Table 1.

2.2. Preparation and treatment of catalysts

AC grains were dried at 100 °C for 6 h in vacuum oven (0.9 kPa) before the arylation. The main properties of AC are depicted in the Table 2. The various weight ratios of sulfanilic acid to AC (0.14/1, 0.70/1, 1.40/1, 3.50/1, 7.00/1, 14.00/1) were used to investigate the effect on S content of $ACPhSO_3H$. The reaction mixture consisting of AC (1.0 g), sulfanilic acid, NaOH and deionized water (50–200 ml) was stirred (magnetic stirrer, 300 rpm) and heated or cooled to pre-determined temperature (20, 30, 50, 70, 85 °C) in 200–800 ml beaker. $NaNO_2$ was added to the reaction mixture after the stoichiometric neutralization of sulfanilic acid with NaOH was completed. The pre-determined amounts of all reactants were calculated based on a mass of sulfanilic acid. The molar ratio of sulfanilic acid to NaOH (1.05), $NaNO_2$ (1.00) and HCl (3.00) was used. The various amounts of water were used to achieve complete solubilisation of reagents at different reaction temperatures. The pH of reaction mixture was controlled in range from 7 to 8 by addition of NaOH. Then, 25% of aqueous HCl was gradually added to the reaction mixture over ≤5 min (depending on the pre-determined temperature, to avoid spontaneous rise of reaction temperature). Excess amount of HCl sometimes is necessary for the compensation of its loss upon evaporation at higher reaction temperatures. From this point of reference, the reaction time (10 min) of arylation of AC was measured. Obtained $ACPhSO_3H$ was removed by decantation and washed with deionized water to neutral pH and then refluxed with acetone in Soxhlet extractor for 3 h. After separation and purification, $ACPhSO_3H$ was dried at 65 °C for 6 h in vacuum oven (0.9 kPa).

The Amberlyst-15 was immersed in methanol for 12 h at room temperature before catalytic tests. Every experiment was repeated twice and S content of $ACPhSO_3H$ and the conversion of RFA to rapeseed oil methyl esters (RME) were determined as average arithmetic from two independently repeated experiments. A third independent experiment was performed in cases when previous two experimental values differed more than 5 wt.%, then the average result of experiment was determined using two closest experimental values. In the similar manner, results of all quantitative analysis data were obtained and the maximum deviation of not more than 3.0% was allowed.

2.3. Characterization of catalyst

Thermogravimetric analysis (TG) of AC and $ACPhSO_3H$ was carried out by simultaneous thermal analyzer (STA) 6000 (PerkinElmer). Experiments were conducted using nitrogen flow

Table 1
The main characteristics of rapeseed oil fatty acids (RFA) and rapeseed oil (RO).

Property	Value	
	RFA	RO
Monoglycerides, wt.%	0.8	0.3
Diglycerides, wt.%	0.9	0.7
Triglycerides, wt.%	0	97.9
Saponification value, mg KOH/g	N.A.[a]	191.71
Acid value, mg KOH/g	199.91	0.01
Fatty acid composition of RO, wt.%		
Palmitic acid (C16:0)	4.1	
Stearic acid (C18:0)	1.4	
Oleic acid (C18:1)	62.5	
Linoleic acid (C18:2)	21.7	
α–Linolenic acid (C18:3)	8.7	
Arachidic acid (C20:0)	0.4	
Other fatty acids	1.2	

[a] Not analyzed.

Table 2
Textural properties, acidity and S content of activated carbon (AC), 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$) and Amberlyst-15.

	S_{BET}[b], m^2/g	V[c], cm^3/g	D[d], nm	S content, mmol/g	Total acid density mmol H^+/g	$PhSO_3H$ density mmol H^+/g
AC	605	0.75	4.9	0.20	0.22	0
$ACPhSO_3H$	114	0.29	10.1	0.91	0.98	0.72
Amberlyst-15	40	0.33	32.9	4.64	4.73	4.64

[b] Specific surface area.
[c] Pore volume.
[d] Average pore diameter.

rate 10 ml/min, heating rate 10 °C/min at maximum temperature 900 °C.

Fourier transform infrared (FT-IR) absorbance spectra of AC and $ACPhSO_3H$ in the range of 500–4000 cm^{-1} were recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Scientific) using KBr pellets.

S content was determined by EA3000 elemental analyzer (Euro Vector). N_2 sorption analysis was performed on a Quadrasorb SI surface area and pore size analyzer at −195.85 °C (Quantachrome Instruments). The AC, $ACPhSO_3H$ and Amberlyst-15 were dried and degassed at 65 °C and 100 °C for 12 h in vacuum oven (10 Pa) using P_2O_5 as water adsorbent before N_2 sorption analysis. The specific surface area was determined using multipoint Brunauer–Emmett–Teller (BET) method based on the adsorption data in the relative pressure (P/P_0) range 0.05–0.31. Pore size distribution (PSD) was evaluated using method, based on the density functional theory (DFT). The total pore volume was estimated from the amount of N_2 adsorbed at a P/P_0 of 0.99 ± 0.01.

The surface morphology of the catalyst was investigated by a field emission scanning electron microscope (FE-SEM) MIRA LMU (Tescan). FE-SEM was operated at 30.0 kV of an accelerating voltage.

Powder X-ray diffraction (XRD) patterns were recorded on an Ultima+ diffractometer using Cu Kα radiation at 40 kV and 20 mA (Rigaku). The samples were scanned in the range of 2θ of 5–60° at a scanning speed of 1°/min.

Total acid density of AC, $ACPhSO_3H$ and Amberlyst-15 were determined using acid-base back titration method [18,22]. Typically, the 0.2 g of sample and aqueous solution of NaOH (30 ml, 0.1 M) were mixed (magnetic stirrer, 300 rpm) at 50 °C for 1 h in 50 ml Erlenmeyer flask. After adding all components, the flask was purged with argon. Then the sample was filtered and washed with deionized water (100 ml) several times. Obtained filtrate was diluted to 150 ml with deionized water. Afterwards, 15 ml of diluted filtrate was titrated with aqueous HCl (0.01 M) using phenolphthalein as an indicator.

The $PhSO_3H$ density of Amberlyst-15 was calculated from the S content. Furthermore, the $PhSO_3H$ density of $ACPhSO_3H$ was calculated from difference of S content between $ACPhSO_3H$ and AC [18,21].

Sulfanilic acid and aromatic compounds (formed from 4-sulfobenzenediazonium chloride) with strong acid properties adsorbed onto AC or $ACPhSO_3H$ surface can significantly affect or mislead the catalytic test results of RFA esterification reactions. Therefore, in order to evaluate the adsorption capacity of acidic aromatic compounds onto carbon materials surface the 50 ml of aqueous solution of sulfanilic/benzenesulfonic acid (molar ratio 1/1, 0.1 M) was stirred (magnetic stirrer 300 rpm) with 0.1 g of AC/$ACPhSO_3H$ mixture (weight ratio 1/1) at 65 °C for 1 h. Then AC/$ACPhSO_3H$ mixture was separated, washed, refluxed and dried in similar manner as in catalyst preparation. S content of AC/$ACPhSO_3H$ mixture before and after treatment with sulfanilic/benzenesulfonic acid was determined.

2.4. Catalytic tests

The catalytic effect of $ACPhSO_3H$ on esterification reactions of RFA and RFA/RO mixture (weight ratio 1/2) were investigated using molar ratio of RFA to methanol (1/20). Utilized amounts of methanol for all esterification reactions were calculated based on acid value (AV) of RFA (Table 1). Esterification reactions were carried out in 250 ml three-neck round-bottom flask equipped with reflux condenser. In all experiments, methanol was stirred (magnetic stirrer, 300 rpm) with $ACPhSO_3H$ (3 g, 10 wt.%) and heated to pre-determined temperature (65 °C). Then, 30 g of RFA or RFA/RO mixture were added to the reaction mixture for ≤0.05–0.10 min. From this point of reference, the reaction time of esterification reactions of RFA was measured. During the esterification reaction, 1.0 ml of sample after 1, 2, 3, 5 and 7 h was taken from reaction mixture using 1.0 ml plastic pipette with filter to separate $ACPhSO_3H$ from the sample (RFA, RO, RME, methanol and water mixture). Then, the sample was dried in vacuum oven (0.9 kPa) at 90 °C for 30 min in order to remove residual methanol and water. The ester content of RME and AV of dry sample were determined. Under similar conditions esterification experiments were conducted using Amberlyst-15.

2.5. Chemical stability and regeneration of catalyst

To investigate the chemical stability of $PhSO_3H$ groups attached onto AC matrix, esterification reactions were carried out seven times with the same catalyst 10.0 wt.% of RFA/RO mixture (weight ratio 1/2, 50 g). The molar ratio of RFA to methanol (1/20), reaction temperature (65 °C), reaction time (2 h) and stirring speed of 300 rpm were used. After each reaction cycle, the $ACPhSO_3H$ was filtered from reaction mixture, washed with HCl (1 M) and acetone at least five times. $ACPhSO_3H$ was dried in vacuum oven (0.9 kPa) at 65 °C for 3 h. After each reaction cycle the S content of dry sample was determined to investigate the elimination of $PhSO_3H$ groups. Then purified $ACPhSO_3H$ was used for the next esterification reaction cycle.

To evaluate the recycling potentials of $ACPhSO_3H$ after the third, fifth and seventh reaction cycle spent catalyst was regenerated. The regeneration of $ACPhSO_3H$ was carried out using preparation methodology of the catalyst, including washing and refluxing step with acetone in Soxhlet extractor for 3 h before arylation of AC.

2.6. Characterization of feedstock and determination of rapeseed oil fatty acid methyl esters content

Monoglycerides, diglycerides and triglycerides content in RO and RFA was determined by gas chromatography (GC) according to a standard method EN14105. A 7890A GC system (Agilent Technologies) with a capillary column HT DB-5 (15 m × 320 μm × 0.1 μm) and a flame ionization detector (FID) was used. The column temperature program: 50 °C hold for 1 min; 15 °C/min up to 180 °C; 7 °C/min up to 230 °C; 10 °C/min up to 370 °C; hold for 5 min at final temperature. Helium was used as a carrier gas at flow rate 5 ml/min (pressure 80 kPa) and the detector temperature was set 390 °C. Injection volume of sample was 1.0 μl.

Saponification value of RO was determined according to the EN ISO 3657 standard method. AV of main feedstock – RO and RFA used in experiments was determined according to the standard method EN 14104. The AV of RFA/RME and RFA/RO/RME mixtures in catalytic tests were determined in similar manner using reduced amount of the sample (∼0.2–0.4 g).

Fatty acid composition of RO was determined by GC analysis using rapeseed oil fatty acid methyl esters (RME_s) obtained from RO in accordance to the standard method ISO 5509. The fatty acid composition of RME_s and ester content of RFA/RO/RME mixtures were determined using standard method EN14103. The 7890A GC system (Agilent Technologies) equipped with a FID and a HP Innowax capillary column (30 m × 250 μm × 0.25 μm) were used. The column temperature program was set at 200 °C for 25 min and detector temperature at 390 °C. Helium was used as a carrier gas at a flow rate 2 ml/min (pressure 215.5 kPa). Injection volume of sample was 1.0 μl. Fatty acid composition of RME_s was calculated on the basis of peak area ratio of alkyl esters. RME_s peaks were identified by comparison to reference standards. We assumed that RO and RFA have the same fatty acid composition as RME_s.

Ester content of RME was calculated based on the sum of existing fatty acid alkyl esters peak area toward the area of internal standard peak (17 – methyl heptadecanoate).

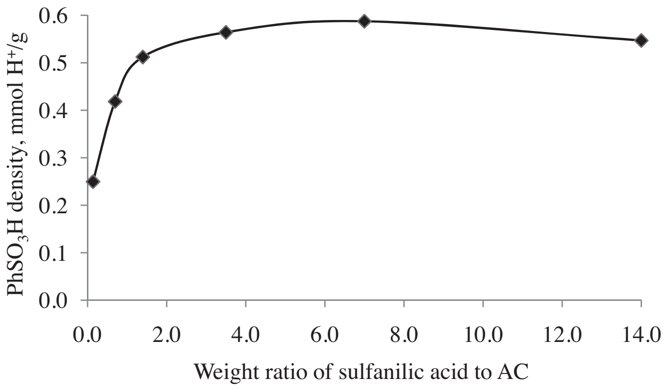

Fig. 1. The effect of weight ratio of sulfanilic acid to activated carbon (AC) on $PhSO_3H$ density of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$). Arylation reaction conditions: reaction time 10 min, reaction temperature 30 °C, stirring speed 300 rpm.

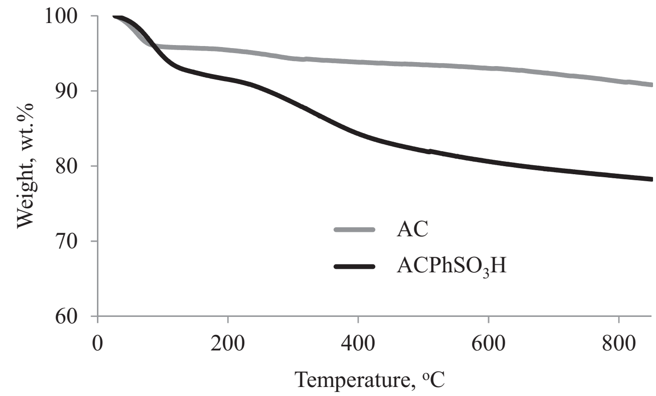

Fig. 3. Thermal stability of activated carbon (AC) and 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$).

3. Results and discussion

3.1. Effect of reaction conditions on catalyst preparation process

The S content of $ACPhSO_3H$ is the appropriate parameter to determine $PhSO_3H$ density of the sample [18,21]. $PhSO_3H$ densities were calculated from the S content and used to govern the catalyst preparation and evaluate the ability of AC to anchor $PhSO_3H$ groups upon arylation.

Fig. 1 shows the effect of weight ratio of sulfanilic acid to AC on $PhSO_3H$ density of $ACPhSO_3H$. The lowest $PhSO_3H$ density (0.25 mmol H^+/g) was obtained using weight ratio of sulfanilic acid to AC (0.14/1). The increase of weight ratio of sulfanilic acid to AC significantly increases $PhSO_3H$ density. The maximum $PhSO_3H$ density (0.59 mmol H^+/g) was reached using weight ratio of sulfanilic acid to AC (7.00/1). Further, increase of weight ratio of sulfanilic acid to AC does not affect the $PhSO_3H$ density of $ACPhSO_3H$.

Fig. 2 shows the effect of reaction temperature on $PhSO_3H$ density of $ACPhSO_3H$. The lowest $PhSO_3H$ density (0.54 mmol H^+/g) was obtained at 20 °C. Increase of the reaction temperature significantly increases the $PhSO_3H$ density. The $ACPhSO_3H$ with maximum $PhSO_3H$ density 0.72 mmol H^+/g using weight ratio of sulfanilic acid to AC (7.00/1) was obtained at 70 °C.

The process of AC arylation with diazonium salts at higher reaction temperature is very complex process and has not been fully explored. A positive impact of higher reaction temperature on the arylation of AC can be attributed with an extent diffusion of reactants through AC matrix and its chemical interaction with active centers of carbon material. On the other hand, a large part of HNO_2 (obtained in $NaNO_2$ reaction with HCl) decomposes to NO, NO_2 (brown gas was visually observed) and water, therefore, having a negative influence on the concentration of 4-sulfobenzenediazonium chloride in reaction mixture. Likewise, the 4-sulfobenzenediazonium chloride intensively reacts with water forming 4-hydroxybenzenesulfonic acid and other by-products. These factors adversely affect the arylation of AC decreasing $PhSO_3H$ density of obtained catalyst as it was observed at 85 °C. However, the highest $PhSO_3H$ density of $ACPhSO_3H$ was reached at optimal temperature (50–70 °C).

3.2. Characterization of catalyst

The main characteristics of AC, Amberlyst-15 and obtained $ACPhSO_3H$ with the highest $PhSO_3H$ density are shown in Table 2. The TG curves of AC and $ACPhSO_3H$ showed low weight loss (~5–7 wt.%) at temperature below ~120 and ~150 °C, respectively (Fig. 3). Observed weight loss indicates the presence of adsorbed water in the samples. The TG analysis showed further weight loss for both samples at higher temperature. Insignificant weight loss (~1 wt.%) of AC sample at temperature range ~120–300 °C refers to the elimination of various oxygen containing groups in AC. Significantly higher weight loss (~8.5 wt.%) of $ACPhSO_3H$ sample at temperature range from ~150–400 °C was observed upon thermal decomposition and desorption of SO3H and PhSO3H groups. Gradual weight loss of $ACPhSO_3H$ at higher temperature ≥400 °C shows further elimination of these groups in comparison with AC. Similar observations were described in the study [18].

In the FT-IR spectra of $ACPhSO_3H$, the S=O stretching vibration bands at 1027 cm^{-1} and 1180 cm^{-1} were identified, indicating

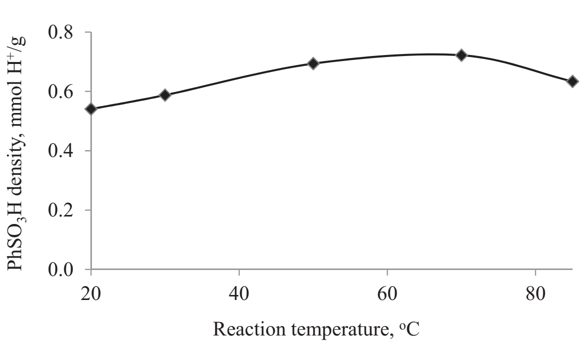

Fig. 2. The effect of reaction temperature on $PhSO_3H$ density of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$). Arylation reaction conditions: weight ratio of sulfanilic acid to activated carbon (AC) 7.00/1, reaction time 10 min, stirring speed 300 rpm.

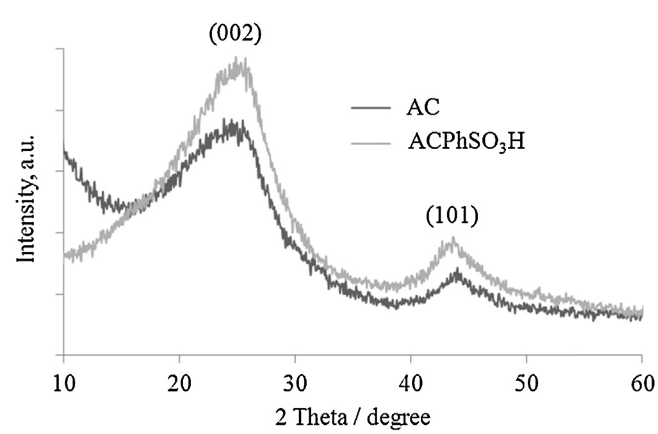

Fig. 4. X-ray diffraction patterns of activated carbon (AC) and 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$).

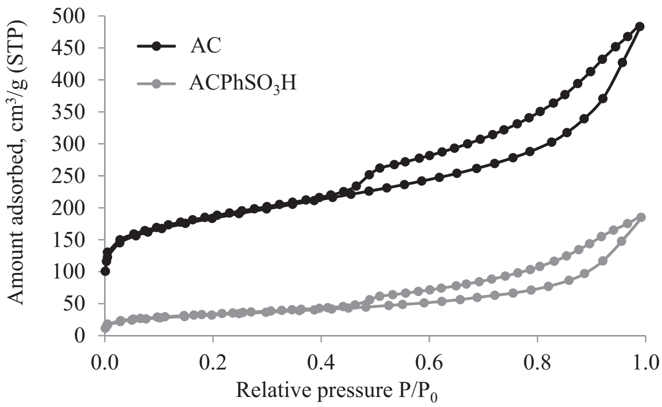

Fig. 5. N_2 sorption isotherms of of activated carbon (AC) and 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$).

to the presence of SO_3H groups on the catalyst surface. These stretching vibration bands were not observed in AC FT-IR spectra. Similar FT-IR absorbance spectra of C_{sac} were described in the paper [21]. Furthermore, the AC/$ACPhSO_3H$ adsorption capacity tests of sulfanilic/benzenesulfonic acid showed insignificant increase of S content (≤0.2 wt.%) of AC/$ACPhSO_3H$ mixture after treatment with aqueous solution of sulfanilic/benzenesulfonic acid (0.1 M) and following washing and refluxing step with water and acetone. This test showed that adsorbed compounds with a similar chemical structure as $PhSO_3H$ groups after intensive treatment were removed from AC and $ACPhSO_3H$ matrix.

Obtained results and observations suggest that $PhSO_3H$ groups after arylation are successfully introduced onto catalyst matrix, but not adsorbed. Fig. 4 shows the XRD patterns of AC and $ACPhSO_3H$. The appearance of broad (0 0 2) and (1 0 1) diffraction peaks in the range of 2θ ~15–35° and ~40–50° attributes the randomly arranged amorphous carbon structures containing low content of crystalline graphite [21,23]. There is no significant difference in the XRD patterns between AC and $ACPhSO_3H$. This means that the influence of arylation process on the microstructure of AC materials is rather negligible [18].

Fig. 5 illustrates the sorption isotherms of AC and $ACPhSO_3H$ with evident hysteresis loops in the P/P_0 range of ~0.44–0.99. The textural properties of AC and $ACPhSO_3H$ are summarized in Table 2. After arylation, the specific surface area and pore volume of $ACPhSO_3H$ dramatically decreased by ~81% and ~61%, respectively, in comparison to AC. This indicates the successful attachment of $PhSO_3H$ groups onto AC matrix, including partial occupation and obstruction of pore space of carbon material.

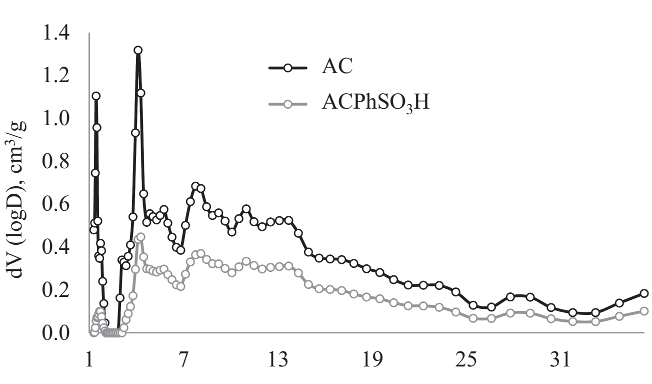

Fig. 6. Pore size distribution (PSD) of activated carbon (AC) and 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$).

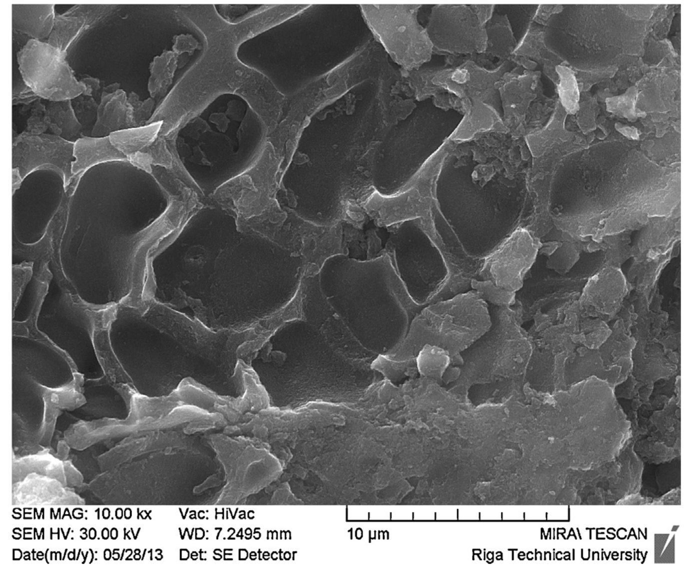

Fig. 7. FE-SEM images of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$).

Furthermore, the average pore diameter of $ACPhSO_3H$ increased more than two times. Reduction of the pore space with lower pore diameter than ~4 nm occurred more intensively than in the case with larger diameter pores increasing the average pore diameter of $ACPhSO_3H$ in comparison with AC (Fig. 6). The PSD of $ACPhSO_3H$ clearly refers to the mesoporous structure of the catalyst.

FE-SEM images (Fig. 7) of the $ACPhSO_3H$ showed that the catalyst also contains a macropores. The textural properties of obtained $ACPhSO_3H$ are capable to provide a successful diffusion of glycerides, FFA and methanol through catalyst matrix due to the average molecular size of these compounds and are roughly ≤4 nm [21].

3.3. The catalytic performance of 4-sulfophenyl activated carbon based solid acid catalyst on conversion of rapeseed oil fatty acids

The conversion of RFA to RME in presence of $ACPhSO_3H$ is shown in Fig. 8. The results obtained under identical reaction conditions using Amberlyst-15 also are shown for comparison. The conversion of RFA in the esterification reaction was quite similar for both catalysts and reached ~95 % after 7 h of reaction. The conversion of RFA

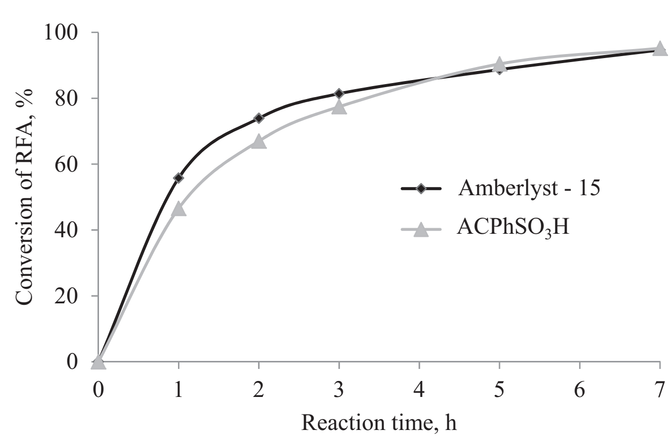

Fig. 8. Esterification of rapeseed oil fatty acids (RFA) in presence of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$) and Amberlyst-15. Esterification reaction conditions: molar ratio of RFA to methanol 1/20, amount of catalyst 10 wt.%, reaction temperature 65 °C, stirring speed 300 rpm.

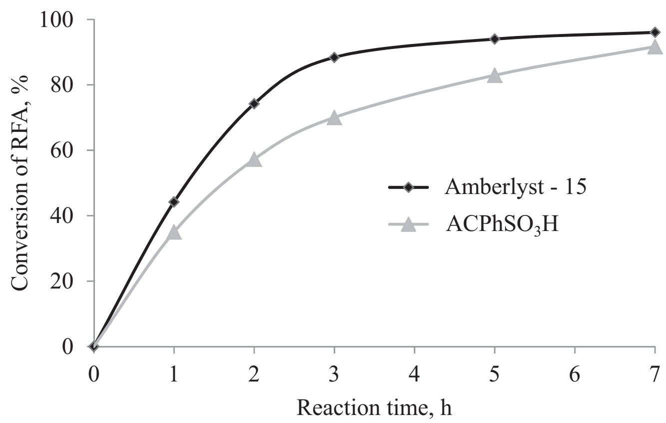

Fig. 9. Esterification of rapeseed oil fatty acids (RFA)/rapeseed oil mixture (weight ratio 1/2) in presence of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$) and Amberlyst-15. Esterification reaction conditions: molar ratio of RFA to methanol 1/20, amount of catalyst 10 wt.%, reaction temperature 65 °C, stirring speed 300 rpm.

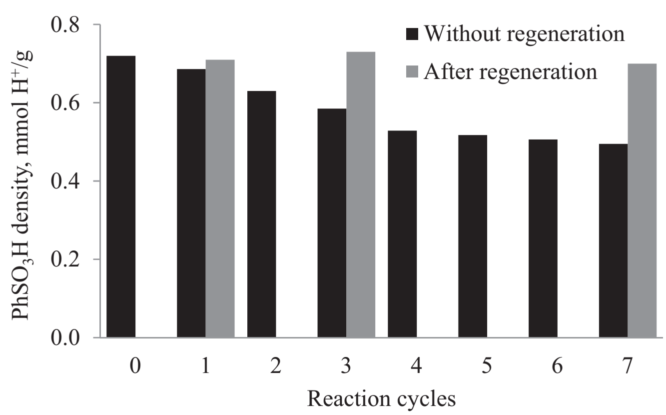

Fig. 10. Chemical stability and regeneration of 4-sulfophenyl activated carbon based solid acid catalyst ($ACPhSO_3H$) after esterification of rapeseed oil fatty acids (RFA)/rapeseed oil mixture (weight ratio 1/2). Esterification reaction conditions: molar ratio of RFA to methanol 1/20, amount of catalyst 10 wt.%, reaction time of cycle 2 h, reaction temperature 65 °C, stirring speed 300 rpm.

at the beginning of the esterification reaction to ~4 h was higher by ~6–9% using Amberlyst-15 as catalyst.

The conversion of RFA (~96%) using RFA/RO mixture in presence of Amberlyst-15 was by 4.5% higher after 7 h than that obtained over the $ACPhSO_3H$ (Fig. 9). Furthermore, reaction rate at the beginning of esterification reaction was higher when Amberlyst-15 was used as catalyst. This can be explained with significantly higher $PhSO_3H$ density of Amberlyst-15 in comparison with $ACPhSO_3H$ (Table 2). High amount of water that forms during reaction adversely affects the overall equilibrium of esterification reaction. Therefore, the esterification curves showed decrease of reaction rate and relatively similar RFA conversion at the end of reaction. Obtained results indicated that $ACPhSO_3H$ catalysed conversion of RFA using pure RFA and RFA/RO mixture was close to Amberlyst-15 after ~4 and ~7 h of reaction. Ester content and AV of the RFA/RO/RME mixtures after catalytic tests showed that transesterification reaction of RO under studied experimental conditions does not occur.

3.4. Chemical stability and regeneration of catalyst

The chemical stability of $PhSO_3H$ groups of the catalyst through seven reaction cycles reusing the same catalyst is shown in Fig. 10. The gradual leaching of $PhSO_3H$ groups from AC matrix after each esterification reaction cycle of RFA/RO mixture was observed. The $PhSO_3H$ groups of $ACPhSO_3H$ decreased by ~32% (0.49 mmol H^+/g) after seventh reaction cycle. The leaching of the $PhSO_3H$ groups from $ACPhSO_3H$ is the main problem of this type AC based solid catalysts [18]. Furthermore, to investigate the recycling possibility of the spent catalyst, it was regenerated after three freely chosen reaction cycles. After regeneration the $PhSO_3H$ density of renewed $ACPhSO_3H$ increases to 0.70–0.73 mmol H^+/g, which is close to freshly prepared catalyst. This leads to conclusion that complete arylation of AC matrix was occurred and maximum $PhSO_3H$ density was achieved. The simple and efficient regeneration method of the spent $ACPhSO_3H$ increases its application potential for biodiesel preparation from feedstock with high content of FFA.

4. Conclusions

The effect of weight ratio of sulfanilic acid to AC and reaction temperature has a significant impact on $PhSO_3H$ density of $ACPhSO_3H$. The $ACPhSO_3H$ with average pore diameter (10.1 nm), specific surface area (114 m^2/g), pore volume (0.29 cm^3/g), and $PhSO_3H$ density (0.72 mmol H^+/g) was obtained. $ACPhSO_3H$ catalysed conversion of RFA to RME using pure RFA and RFA/RO mixture was close to Amberlyst-15 and reached ~95 and ~92 % after 7 h of reaction, respectively. The simple and efficient regeneration method of spent $ACPhSO_3H$ and high catalytic performance of the catalyst on conversion of RFA increases its application potential for biodiesel preparation from feedstock with high content of FFA.

Acknowledgement

Support for this work was provided by the Riga Technical University through the Scientific Research Project Competition for Young Researchers No. ZP-2014/1.

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